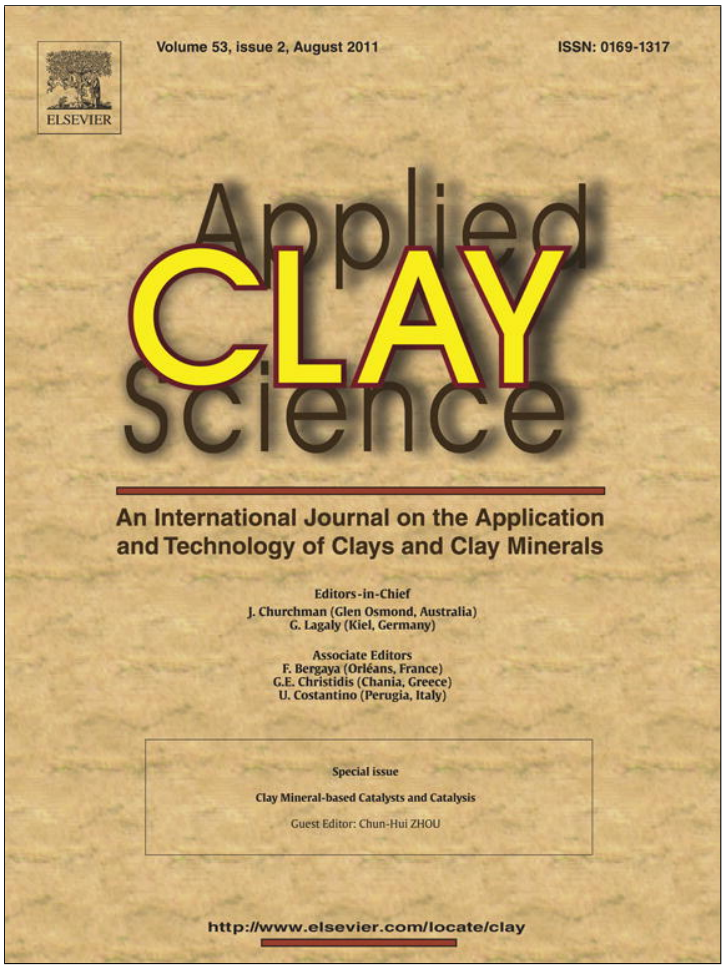

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Note

Activated clay supported heteropoly acid catalysts for esterification of acetic acid with butanol

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ABSTRACT

The esterification of acetic acid with primary (*n*-), secondary (*sec*-) and tertiary (*ter*-) butanol catalyzed by supported heteropoly acids (HPAs), such as dodecatungstophosphoric acid (TPA), dodecatungstosilicic acid (TSA) and dodecamolybdophosphoric acid (MPA) on acid activated Bentonite (AT-GMB) matrix have been carried out. The 20% loaded TPA on AT-GMB showed the highest catalytic activity. The conversions of different alcohols into the corresponding esters decrease in the following order: *n*-butanol>*sec*-butanol>*ter*-butanol. The selectivities for the corresponding esters are nearly 100%. The catalysts were characterized by surface area, thermal analysis, XRD and FTIR spectroscopy. The reusability study shows that the catalysts are stable and active.

1. Introduction

Esters, which include a wide category of organic compounds ranging from aliphatic to aromatic, are generally used as plasticizers, solvents, perfumes, flavor chemicals and also as precursors for a gamut of pharmaceuticals, agrochemicals and other fine chemicals (Zaidi et al., 1995). Compared to primary alcohols, esterifications of secondary and tertiary alcohols are much more difficult to achieve. The steric effect of the substrates and less nucleophilicity of the oxygen atom hinders the formation of the corresponding ester (Shih et al., 1997). Apart from esterification, the formation of light alkenes (e.g. 1- and 2-butene) and dibutyl ether as byproducts also occurred. In the presence of an acid catalyst, *ter*-butanol undergoes dehydration to *iso*-butylene even at room temperature (Niasari et al., 2005). Despite the strong catalytic effect, the use of homogeneous catalysts like sulphuric acid, *p*-toluenesulphonic acid etc. suffers from several drawbacks, such as the occurrence of side reactions, corrosion of the equipment and the need to deal with acidic wastes (Kantam et al., 2002; Liu and Tan, 2001). Such homogeneous catalysts may also result in sulphur contamination of the final ester product (Harmer and Sun, 2001). Therefore, the use of solid catalysts has received increasing attention (Liu and Tan, 2001). Many heterogeneous catalysts reported in the literature for esterification include ion exchange resin (Gimenez et al., 1987), H-ZSM-5 (Zhang et al., 1992), zeolites-Y (Corma et al., 1989), niobic acid (Chen et al., 1984), sulphated oxides (Hino and Arata, 1981), heteropoly acid supported clay (Bhorodwaj and Dutta, 2010; Bhorodwaj et al., 2009), and metal ion exchanged montmorillonite (Ramesh et al., 2010).

Heteropoly acids (HPAs) with a Keggin structure are widely used as acid catalysts due to their very strong Brønsted acidity and structural properties (Haber et al., 2003). The Keggin-type HPAs, typically represented by the formula $H_{8-x}[XM_{12}O_{40}]$, where X is the heteroatom (most frequently P^{5+} or Si^{4+}), *x* is its oxidation state, and M is the addenda atom (usually W^{6+} or Mo^{6+}) are the most important for catalysis (Kozhevnikov, 2003). The HPAs like $H_3[PW_{12}O_{40}]$ (TPA), $H_4[SiW_{12}O_{40}]$ (TSA) and $H_3[PMo_{12}O_{40}]$ (MPA) are readily available and most frequently used as acid catalysts. The catalytic activities of these acids, both in homogeneous and heterogeneous systems, usually depend on their acid strength, i.e. TPA>TSA>MPA (Kozhevnikov, 1998). TPA, being the strongest acid, acted as an efficient proton donor and therefore exhibited higher catalytic activity than the other two HPAs, (Kozhevnikov, 1998). These acids have fairly high thermal stabilities, decomposing at 465, 445 and 375 °C respectively. In homogeneous liquid phase catalysis, the advantages of the HPAs are more distinctive due to their low volatility, low corrosiveness, high acidity, activity and flexibility. Depending on the reaction conditions, the activity / mole proton of HPA may be higher by a factor of 3—100 times than sulphuric acid as far as reactivities in Brønsted acid-catalysed liquid phase reactions are concerned (Yadav, 2005). But, the main disadvantages of HPAs as catalysts lie in their relatively low surface area (1–10 m^2/g) and the problem of separation from the reaction mixture (Kozhevnikov, 2002; Sawant et al., 2007; Timofeeva et al., 2004). HPAs on suitable support are expected to overcome the above mentioned problems. A number of porous supports with high surface areas such as silica, ZrO_2, active carbon, SBA-15, zeolite (Chimienti et al., 2001; Liu et al., 2004; Mukai

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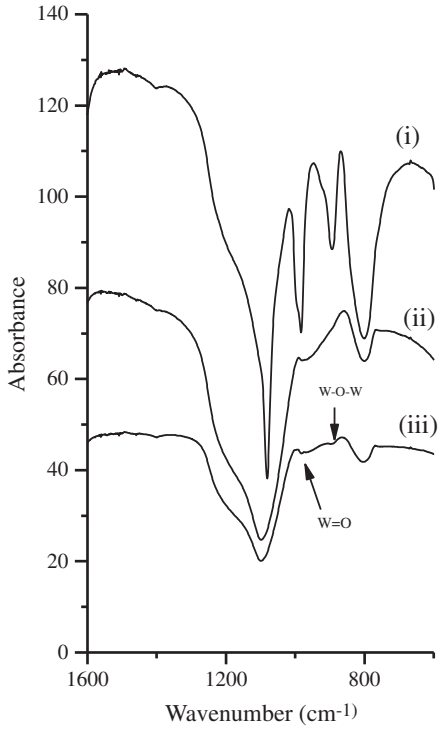

Fig. 1. FTIR spectra of (i) pure TPA, (ii) AT-GMB and (iii) 20 wt.% TPA / AT-GMB.

et al., 2003; Sepulveda et al., 2005; Shikata et al., 1997; Timofeeva et al., 2002), have been used for supporting HPAs.

Clay-based materials have attracted great attention because of their applications from traditional ceramics to modern functional nanocomposites (Zhou, 2010). Depending on the layer structure and specific properties, advanced clay-based materials have been widely used in paper industries, pharmaceuticals, catalysts or catalyst supports and decolorizing agents (Tong et al., 2010; Zhang et al., 2010) etc. Acid modified clay mineral can be used as an efficient support for HPAs (Ahmed and Dutta, 2003a; Bhorodwaj and Dutta, 2010; Bhorodwaj et al., 2009) because they exhibit high surface area, pore volume, pore diameter and higher surface acidity (Ahmed and Dutta, 2005; Hart and Brown, 2004). The acid strengths of HPA supported on some of the materials mentioned above were found to be lower than that of bulk HPA due to the interaction of HPA with surface functional groups of supports. But uniform dispersion of HPAs on porous acid activated Bentonite support with high surface area increases the overall acidity and catalytic activity of the composites. In view of the above, the present study aims at the synthesis of the solid acid catalysts by supporting different heteropoly acids, such as TPA, TSA and MPA on an acid activated Bentonite (AT-GMB) matrix having high surface area prepared from Bentonite by HCl acid activation and to evaluate their catalytic activities towards esterification of acetic acid using various alcohols such as primary (*n*-), secondary (*sec*-) and tertiary (*ter*-) butanol. The process provides a simple ecofriendly operation since there is no effluent disposal problem associated with it.

2. Experimental

2.1. Support preparation

Raw clay (Bentonite) [Gujarat Mines Bentonite (GMB), India] that contained silica sand, iron oxide, etc. as impurities was purified by a standard sedimentation method (Gillott, 1968) to collect the <2 μm fraction before use. The oxide composition of the clay as determined by chemical and flame photometric methods were SiO_2: 49.42; Al_2O_3: 20.02; Fe_2O_3: 7.49; MgO: 2.82; CaO: 0.69; LOI: 17.51; others (Na_2O, K_2O and TiO_2) 2.05%.

The purified clay (1 g) was refluxed with 4 M HCl acid (100 ml) for 15 min. The slurry was cooled, filtered and washed thoroughly with water and was dried in an air oven at 393 K for 12 h (Ahmed and Dutta, 2005; Phukan et al., 2003). The clay samples thus prepared were designated as AT-GMB.

2.2. Catalyst preparation

A series of catalysts having 10, 20 and 30% loading of different HPAs (Aldrich, 99.9%) on AT-GMB were synthesized. HPAs were supported on AT-GMB by means of the incipient wetness impregnation method (Haber et al., 2003). A known amount of HPA was dissolved in water and the hot support (dried at 120 °C for 6 h in an oven) was added to the solution. The slurry was shaken for 15 min at room temperature, washed with water and dried in the oven at 373 K for 12 h. They are each designated as wt.% HPA / AT-GMB.

2.3. Characterization techniques

The bulk HPAs as well as supported on AT-GMB catalysts were characterized by FTIR analysis using a Perkin-Elmer system 2000 FTIR spectrometer.

Specific surface area and pore volume were measured by using an Autosorb1 (Quantachrome, USA). Specific surface area of the catalyst samples was determined by using the Brunauer–Emmett–Teller (BET) method. N_2 vapour adsorption data were obtained for the vapour pressure range (p/p_o) of 0.03 to 0.3. Prior to adsorption, samples were degassed at 200 °C for about 1.5 h.

The TG-DTA measurements of the samples were made with the Thermal Analyzer (TA instruments, Model STD 2960 simultaneous DTA-TGA) with about 10 mg of sample in a platinum crucible at a heating rate of 10 °C min^{-1} in an air atmosphere.

Table 1
Surface properties, effects of loading and reusability of different catalysts on esterification.

Catalysts	*n*-butanol		*sec*-butanol		*ter*-butanol		BET surface area (m^2/g)	Total pore volume (cm^3/g)
	Conversion (%)	TOF (min^{-1})	Conversion (%)	TOF (min^{-1})	Conversion (%)	TOF (min^{-1})		
10% TPA/AT-GMB	79	129	52	85	17	28	140	0.15
20% TPA /AT-GMB	88[a]	141	80[a]	129	45[a]	72	120	0.12
	79[b]	131	74[b]	118	36[b]	56		
	76[c]	125	68[c]	102	31[c]	52		
30% TPA /AT-GMB	76	123	49	64	23	37	100	0.10
20% TSA /AT-GMB	84	138	60	99	22	36	112	0.11
20% MPA /AT-GMB	80	134	52	87	12	20	109	0.09

Reaction conditions: temperature: 150 °C, catalyst amount: 0.3 g, acid: alcohol: 3:1 (mole ratio), reaction time: 12 h.
[a] 1st run.
[b] 2nd run.
[c] 3rd run.

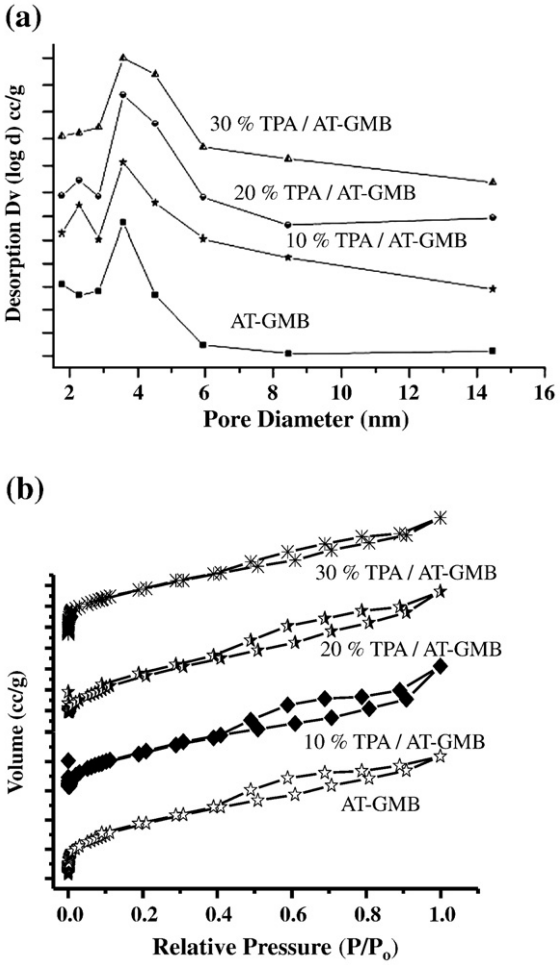

Fig. 2. (a) Pore size distribution curves of different samples determined by applying BJH method. (b) N_2 adsorption–desorption isotherms for AT-GMB and 30% TPA / AT-GMB.

XRD patterns of AT-GMB and different wt% of TPA on AT-GMB samples were taken in the range $2\theta = 2–60^o$ at a rate of 1^o/min (X-ray diffractometer JEOL, JDX-11p 3A, Japan).

2.3.1. Spectral data

IR (KBr): 1080 [P–O in central tetrahedral], 984 cm^{-1} [terminal W = O], 894, 801 cm^{-1} [W–O–W] cm^{-1} (*Bulk TPA*); 978 [W–O], 915 [Si–O], 885 and 798 [W–O–W] cm^{-1} (*Bulk TSA*); 1061 [P–O], 961 [Mo = O (terminal oxygen)], 861 and 776 cm^{-1} [Mo–O–Mo (corner-sharing and edge-sharing bridging oxygen)] (*Bulk MPA*); 1082 [Si–O], 918 [AlAlOH], 880 [AlFeOH], 843 [AlMgOH], 798 [Si–O (amorphous silica)] cm^{-1} (*AT-GMB*).

2.4. Esterification reactions

0.3 g of freshly activated catalyst (dried at 120 °C for 2 h in an oven), 0.15 mol of acetic acid (Merck, 99.8%), 0.05 mol of corresponding butanol (Merck, 98%) were taken into a pressure autoclave. The autoclave temperature was then slowly raised to 150 °C (autogeneous pressure 1–3 atm) and maintained at this temperature during the specified reaction periods (1–12 h). The reaction products were collected from the autoclave and analyzed by GC (Chemito GC, Model 8510, FID). The catalysts were washed with water and activated for the next experiments.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. FTIR

Bulk TPA showed the characteristic IR bands at 1080 cm^{-1} (P–O in central tetrahedral), 984 cm^{-1} (terminal W = O), 894 and 801 cm^{-1} (W–O–W) associated with the asymmetric vibrations of the Keggin polyanion. Upon being supported on AT-GMB, some of the characteristic Keggin bands were observed at 982 cm^{-1} and 893 cm^{-1} and other bands were merged in with the AT-GMB bands (Fig. 1). Similarly, the bulk TSA showed characteristic IR bands at 978 (W–O), 915 (Si–O), 885 and 798 (W–O–W) cm^{-1} and some of them were also detected in the loaded catalysts but with considerably lower intensity. Likewise, MPA showed P–O, Mo = O (terminal oxygen), and the two Mo–O–Mo (corner-sharing and edge-sharing bridging oxygen) bands at 1061, 961, 861 and 776 cm^{-1} respectively and a few of them were also observed in the loaded catalysts with less intense bands.

3.1.2. Nitrogen adsorption

The surface area and pore volume of AT-GMB and HPAs loaded AT-GMB were measured and it appeared that, in general, the surface area and pore volume of AT-GMB were reduced considerably upon loading with different HPAs. The results of a typical example i.e. TPA / AT-GMB catalysts are given in Table 1. The surface area (340 m^2/g) and the total pore volume (0.49 cm^3/g) of AT-GMB decreased as the amount of TPA loading increased and for 30% TPA loading the surface area decreased to 100 m^2/g and the total pore volume reduced to 0.10 cm^3/g only. The high surface area of acid activated clay was related to the removal of the aluminum from octahedral sites in the clay sheet. The reduction in surface area and pore volume upon TPA loading might be due to the blockage of pores by TPA molecules. The pore size distributions, as determined from the desorption branch of the N_2 adsorption isotherm using the Barrett–Joyner–Halenda (BJH) method, [Fig. 2(a)], showed that the average pore sizes of AT-GMB and different weight percents of TPA on AT-GMB were in the range of 3.5–5 nm suggesting that pore sizes of the catalysts were in the mesoporous region, i.e. 2–50 nm. The adsorption–desorption isotherms of AT-GMB and 10–30% TPA / AT-GMB presented in Fig. 2(b) suggested the Type IV isotherms with the hysteresis loop of type H3, which was a characteristic of a mesoporous solid.

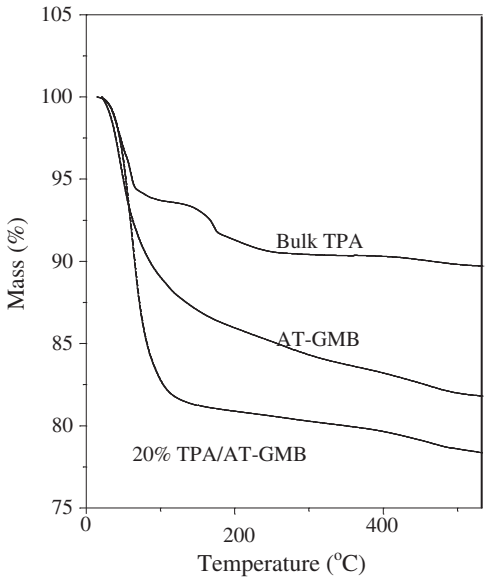

Fig. 3. Thermal analyses of bulk TPA, AT-GMB and 20% TPA / AT-GMB samples.

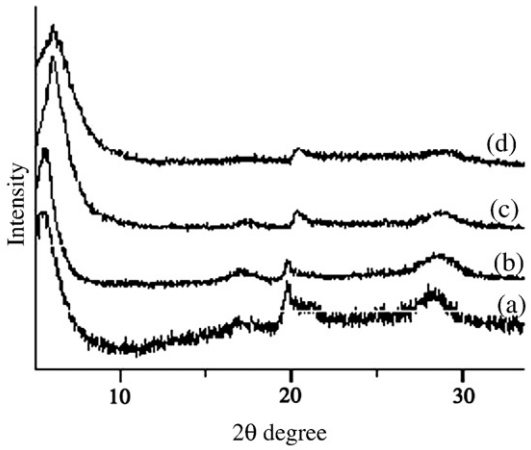

Fig. 4. The XRD patterns of (a) AT-GMB (b) 10% TPA / AT-GMB (c) 20% TPA/AT-GMB (d) 30% TPA / AT-GMB samples.

3.1.3. Thermal analysis

The detailed thermal analyses carried out on bulk TPA, AT-GMB and on 20% TPA / AT-GMB samples (Fig. 3) showed a mass loss of about 8% up to a temperature of 180 °C, indicating loss of free and adsorbed water. The gradual mass loss of about 3% up to 500 °C corresponds to the mass loss due to the reaction between acidic protons and structural oxygen from phosphotungstic acid releasing water followed by decomposition to WO_3 and PO_x species (Bhorodwaj and Dutta, 2010; Bhorodwaj et al., 2009; Newman et al., 2006). The thermal data of AT-GMB showed a steady loss of mass of about 17% up to 500 °C which was attributed to the loss of physisorbed and interlayer water and also due to dehydroxylation caused by the breaking of structural OH-groups of the support (Ahmed and Dutta, 2003b; Bhorodwaj and Dutta, 2010; Bhorodwaj et al., 2009). The TGA of supported TPA onto AT-GMB showed about 18% mass loss within the temperature range of 80–150 °C due to a loss of adsorbed water molecules. A gradual mass loss of about 3% up to 500 °C was also observed, which indicated an increase in the thermal stability of TPA on AT-GMB support. This might be due to the formation of intermolecular bonding between the support and heteropoly acid and indicated the presence of chemical interaction between them (Bhorodwaj and Dutta, 2010; Bhorodwaj et al., 2009; Patel et al., 2003). Similar observations were also made for other HPAs / AT-GMB catalysts.

3.1.4. XRD measurement

The XRD pattern (Fig. 4) of AT-GMB showed a highly intense basal peak at about $2\theta = 5.72^{o}$ corresponding to the basal d-spacing (d_{001}) of about 12.5 Å. Several other peaks were also observed which indicated that AT-GMB was still crystalline in nature. In the diffractograms of different loadings of TPA on AT-GMB, the peaks were observed to be less intense, indicating that during impregnation of TPA on AT-GMB, the clay lost some of its crystallinity compared to AT-GMB. Most of the diffractograms of TPA loaded AT-GMB were observed to be similar to that of AT-GMB, indicating the retention of the original characteristics of AT-GMB.

3.2. Catalytic activity

Earlier experience (Bhorodwaj and Dutta, 2010; Bhorodwaj et al., 2009) and preliminary experiments prompted us to utilize the optimum conditioned catalysts i.e. 20% TPA-, TSA-, MPA / AT-GMB for conducting the esterifications (Table 1). The major product formed was butyl acetate with a selectivity of nearly 100%. The amount of conversion of alcohol depends on the type of catalysts as well as the nature of alcohols used. The highest conversions (Table 1) were found for TPA / AT-GMB catalyst for all types of butanols followed by TSA- and MPA-containing catalysts. A detail study on conversion and selectivity on esterifications with different loading of TPA on AT-GMB was carried out and the results revealed (Table 1) that on increasing the loading from 10 to 20% TPA on AT-GMB, the conversion increased, but thereafter, it decreased on further loading to 30%. The Turn Over Frequencies (TOFs) of the catalysts also followed a similar trend. In our previous studies (Bhorodwaj and Dutta, 2010; Bhorodwaj et al., 2009) it was confirmed that the activity of HPA alone was significantly lower than that of the same amount supported on AT-GMB under the same reaction conditions. The enhanced activity may be ascribed to a high dispersion of the TPA on AT-GMB, providing more surface area and active sites than pure HPA.

Control of water content in HPAs catalysts was essential for their efficient performance. This could be achieved by thermal pretreatment of the catalysts (Ghosh and Moffat, 1986), typically at 130–200 °C. Excess water caused a decrease in the HPA acid strength, and thus lowered its activity. At higher calcination temperatures, dehydration / dehydroxylation of the catalyst occurred (Devassy and Halligudi, 2006) and led to an increase in the acid strength but decreased the number of acid sites, which might reduce the overall catalytic activity (Kozhevnikov, 2003). Therefore, the catalysts were activated at optimum temperature i.e.120 °C before use.

3.2.1. Influence of reaction time

Among the three HPAs, TPA-containing catalyst showed the highest catalytic activities in esterifications (vide supra) and therefore a detailed study on the influence of reaction time on the acetic acid conversion using 20% TPA / AT-GMB catalyst was carried out. A gradual increase in the conversion was observed (Fig. 5) with the increase in reaction period. It revealed that at 9 h reaction time, about 85, 79 and 42% of conversions were observed for *n*-, *sec*- and *ter*-butanol respectively, which were enhanced to 88, 80 and 45% at the end of 12 h. The selectivity towards butyl acetate remained almost 100% in all the cases.

3.2.2. Influence of catalyst amount

The effect of catalyst amount on the esterification of acetic acid with different alcohols for 1 and 12 h showed that (Fig. 5) with the increase in catalyst amount, the conversion increased marginally, which may be due to diffusional resistance in catalyst pores (Bhorodwaj and Dutta, 2010; Bhorodwaj et al., 2009; Lilja et al., 2002). The product molecules remained adsorbed within the pores / channels of the catalyst and may restrict diffusion for the fresh

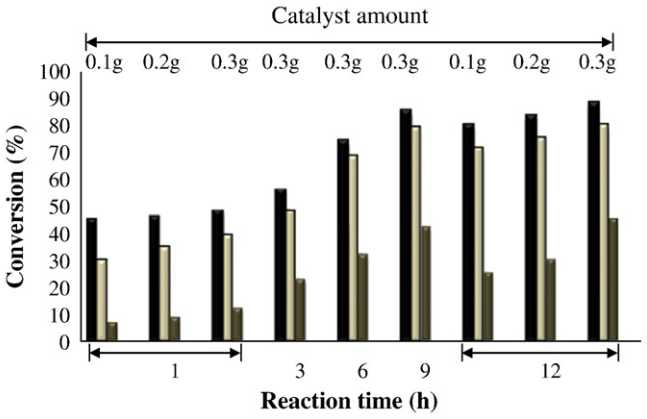

Fig. 5. The effects of reaction time and catalyst amount on the esterification of acetic acid with *n*-, *sec*-, *ter*-butanol. *Reaction conditions*: temperature: 150 °C (closed system), pressure: 3 atm, acid: alcohol: 3:1 (mole ratio).

reactants. The selectivity, however, towards different esters was nearly 100%.

3.3. Recyclability of the catalyst

The regeneration of the catalysts after 12 h reaction time was done by filtration, washing with conductivity water for several times followed by drying at 120 °C in an air oven and they were used in the esterification reactions with a fresh reaction mixture. As a typical example, the catalyst TPA / AT-GMB showed (Table 1) conversion of 88, 80 and 45% for *n*-, *sec*- and *ter*-butanol in the first run, which decreased to about 79, 74 and 36% in the 2nd run and 76, 68 and 31% in the 3rd run respectively. The TOFs also decreased with subsequent reuse. This decrease in catalytic activity was attributed to the leaching of HPA (of about 3–5%) from the support into the liquid phase during the catalytic reactions which was confirmed by the well-known ascorbic acid test (Yadav and Bokade, 1996). The leaching of HPA into the reaction mixture in the course of the reaction was also checked by a hot filtration technique. The reaction was carried out for 2 h under optimized reaction conditions using fresh TPA / AT-GMB catalyst. The reaction was stopped after 1 h and the catalyst was separated by filtration and then the hot filtrate was stirred further for 1 h under the same reaction conditions. In the absence of the catalyst an increase in conversion of about 7% was observed. This also indicated the presence of some amount of HPA in the reaction mixture. Although the catalyst was washed after filtration to remove all the adsorbed reactants and products, the possibility of retention of some of the adsorbed reactants and products species still remained, which might cause the blockage of active sites and cause a decrease in catalytic activity. However, the selectivity remained almost unchanged, i.e. >99.5%.

4. Conclusion

Heteropoly acids (HPA) supported on AT-GMB act as efficient stable solid acid catalysts for esterifications of acetic acid with *n*-, *sec*- and *ter*-butanol to produce their corresponding esters. The high catalytic activities are attributed to the high surface area and Brønsted acid sites of the catalysts. The TPA loaded on AT-GMB showed the highest efficacy while MPA-containing catalyst exhibited the least activity. In all the esterification reactions the selectivity was nearly 100% while the highest conversions were about 88, 80 and 45% for *n*-, *sec*- and *ter*-butyl acetate respectively within 12 h of reaction time for catalyst TPA / AT-GMB. The catalysts can be regenerated and reused for several runs.

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